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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/790,535	03/01/2004	Michael B. Korzenski	ATMI-692	4252
<div>24239      7590      10/18/2007</div> <div>MOORE &amp; VAN ALLEN PLLC</div> <div>P.O. BOX 13706</div> <div>Research Triangle Park, NC 27709</div>				
			EXAMINER	
			DOUYON, LORNA M	
			ART UNIT	PAPER NUMBER
			1796	
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**Please find below and/or attached an Office communication concerning this application or proceeding.**

The time period for reply, if any, is set in the attached communication.

<b>Office Action Summary</b>	Application No. 10/790,535	Applicant(s) KORZENSKI ET AL.	
	Examiner Lorna M. Douyon	Art Unit 1796	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

- 1) ☒ Responsive to communication(s) filed on 16 August 2007.
- 2a) ☐ This action is **FINAL**.                      2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

- 4) ☒ Claim(s) 1-16, 18, 20-41, 43 and 45-63 is/are pending in the application.
- 4a) Of the above claim(s) \_\_\_\_\_ is/are withdrawn from consideration.
- 5) ☐ Claim(s) \_\_\_\_\_ is/are allowed.
- 6) ☒ Claim(s) 1-16, 18, 20-41, 43, 45-54, 56 and 58-63 is/are rejected.
- 7) ☒ Claim(s) 55, 57 is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on \_\_\_\_\_ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.  
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).  
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All    b) ☐ Some \*    c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
  2. ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_\_.
  3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

\* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

- |  |   |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892)                                | 4) <input type="checkbox"/> Interview Summary (PTO-413)<br>Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948)                       | 5) <input type="checkbox"/> Notice of Informal Patent Application                       |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08)<br>Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____  |

***Continued Examination Under 37 CFR 1.114***

1. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on August 16, 2007 has been entered.
2. Claims 1-16, 18, 20-41, 43, 45-63 are pending.
3. The rejection of claims 1-16, 18, 20-41, 43, 45-54, 60-63 under 35 U.S.C. 112, first paragraph is withdrawn in view of Applicants' amendment.
4. The rejection of claim 45 under 35 U.S.C. 112, second paragraph is withdrawn in view of Applicants' amendment.
5. The rejection of claims 56, 58-59 under 35 U.S.C. 103(a) as being unpatentable over Mullee et al. (US Patent No. 6,500,605) in view of Hayasaki et al. (US Patent No. 7,018,481) is withdrawn in view of Applicants' amendment.
6. The rejection of claims 62-63 under 35 U.S.C. 103(a) as being unpatentable over Reid et al. (US Patent No. 6,958,123) is withdrawn in view of Applicants' amendment.

7. The rejection of claim 55 under 35 U.S.C. 103(a) as being unpatentable over DeYoung et al. (US Patent No. 6,669,785) in view of McClain et al. (US Patent No. 6,623,355) in further view of DeYoung et al. (US Patent No. 7,044,143) is withdrawn in view of Applicants' amendment.

***Claim Rejections - 35 USC § 103***

8. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action.

9. Claims 1-12, 14-16, 18, 20, 23-38, 40-41, 43, 45, 48-52, 60-63 are rejected under 35 U.S.C. 103(a) as being unpatentable over Mullee et al. (US Patent No. 6,500,605), hereinafter "Mullee '605" in view of DeSimone et al. (US Patent No. 5,866,005), hereinafter "DeSimone".

Mullee '605 teaches a method of removing photoresist and residue from a wafer following a medium dose ion implant wherein the method begins by maintaining supercritical carbon dioxide, a solvent and aqueous fluoride in contact with the wafer (see col. 4, lines 34-38; 62-64), wherein the solvent used were BLO (butyrolactone), DMSO (dimethyl sulfoxide) and glacial acetic acid, and additional water and the aqueous fluoride was aqueous ammonium fluoride (see col. 11, lines 25-34). The residue includes SiO<sub>2</sub> etch residue or SiN etch residue (see col. 3, lines 15-19). The pressure chamber was maintained at 70°C, the aqueous fluoride and solvent were

circulated for 2 minutes at 1,250 psi after which the pressure chamber was pressurized to 2,800 psi, and two partial exhausts and one full exhaust were employed between the removal and rinse step (see col. 11, lines 25-49). The proportions of the above components are suggested in col. 11, lines 25-33 and 52-58. Mullee '605, however, fails to specifically disclose (1) a binder which is derived from at least one ethylenically unsaturated reactant, for example polyvinyl alcohol or polyvinyl amine, alcohols like methanol and (2) a contacting time in the range from about 4 minutes to about 20 minutes, and pre-cleaning the wafer surface with a SCF-based pre-cleaning composition comprising SCF and an aqueous-based pre-cleaning formulation.

DeSimone, an analogous art, teaches the separation of photoresist contaminant from a substrate (see col. 6, lines 43-52) with carbon dioxide fluid, for example, supercritical carbon dioxide (see col. 2, lines 10-11; 36-52) and amphiphilic species (see abstract; col. 2, lines 29-31). The amphiphilic species is generally present in the carbon dioxide fluid from 0.001 to 30 weight percent (see col. 3, lines 51-53) and contains a CO<sub>2</sub>-philic segment and a CO<sub>2</sub>-phobic segment, which may be covalently joined to the CO<sub>2</sub>-philic segment (see col. 3, lines 53-58). Exemplary CO<sub>2</sub>-philic segments may include a fluorine-containing segment, for example, fluoropolymers and exemplary CO<sub>2</sub>-phobic segments may comprise common lipophilic, oleophilic and aromatic polymers, as well as oligomers (formed from monomers such as ethylene, acrylates, methacrylates, vinyl alcohol, etc), and molecular units containing functional groups such as esters, sulfonic, salts of various acids, amines (see col. 3, line 59 to col. 4, line 38). The amphiphilic species may be in the form of, for example, random, block

and star homopolymers, copolymers and co-oligomers (see col. 4, lines 39-43).

Fluorinated ethoxylates may also be used, and mixtures of any of the above may be used (see col. 4, lines 63-67). The CO<sub>2</sub> fluid also contains a co-solvent like water (see col. 3, lines 8-19), alcohols, e.g. methanol, ethanol, and isopropanol, a co-surfactant, and other additives (see col. 2, lines 53-62; col. 3, lines 20-22). Other additives may be employed in the carbon dioxide and one example is non-surface active polymeric materials such as fluoroalkyl polyacrylics which prevents particle redeposition (see col. 5, lines 27-38). This carbon dioxide fluid which contains amphiphilic species removes a wide range of organic and inorganic materials such as high molecular weight non-polar and polar compounds, along with ionic compounds (see col. 1, lines 52-59; 66-67).

With respect to difference (1), it would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate the amphiphilic species of DeSimone which contains a monomer segment like vinyl alcohol or amine segment, and alcohols, like methanol, into the carbon dioxide fluid of Mullee '605 because this would remove a wide range of organic and inorganic material contaminants as taught by DeSimone.

With respect to difference (2), it would have been obvious to one of ordinary skill in the art at the time the invention was made to reasonably expect the contacting time of the composition of Mullee '605 to be within those recited because the term "about" permits some tolerance, hence, the lower limit of "about 4 minutes" of the present claim may be considered to read on the 2 minutes circulation time in the teachings of Mullee '605 in col. 11, line 35, and to reasonably expect the cleaning method of Mullee '605 to

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read on the pre-cleaning step as well, because a repetition of step is within the level of ordinary skill in the art.

10. Claims 13 and 39 are rejected under 35 U.S.C. 103(a) as being unpatentable over Mullee '605 and DeSimone as applied to the above claims, and further in view of Douglas et al. (US Patent No. 5,868,862), hereinafter "Douglas".

Mullee '605 and DeSimone teach the features as described above. Mullee '605 and DeSimone, however, fail to disclose incorporating into the composition a surfactant such as an anionic surfactant like sodium alkyl sulfates.

Douglas teaches the incorporation of surfactants such as anionic surfactant like sodium dodecyl sulfate into a similar composition comprising supercritical carbon dioxide for removing contaminants overlaying a substrate (see col. 5, lines 37-40).

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate anionic surfactant like sodium dodecyl sulfate into the composition of Mullee '605 and DeSimone because such incorporation would provide increased effectiveness in the removal of contaminants overlaying a substrate as taught by Douglas.

11. Claims 1-16, 18, 20-21, 23-41, 43, 45, 48, 51-54, 60-63 are rejected under 35 U.S.C. 103(a) as being unpatentable over Joyce et al. (US Patent No. 6,764,552), hereinafter "Joyce" in view of DeSimone.

Joyce teaches a supercritical cleaning solution which includes supercritical

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carbon dioxide with a fluoride source, preferably hydrogen fluoride or ammonium fluoride, wherein the fluoride has a final concentration in the supercritical solution of between about 0.1 and 2% by weight, and up to about 20% by weight, preferably between about 2 and 10 percent by weight co-solvents like alcohols like methanol, ethers and water (see col. 13, lines 11-29; col. 7, lines 17-52; col. 9, lines 18-20). The supercritical solution may include up to about 15% by weight, preferably between about 0.1 and 2% by weight chelating agent like EDTA, up to about 5% by weight anti-corrosion agent (wherein both can read on surface passivator), and further includes up to about 50%, preferably between about 0.1 and 30% by weight of a surfactants like anionic, cationic or neutral surfactants, for example, amphiphilic fluoropolymers (see col. 13, lines 35-49; col. 9, lines 57-61; col. 10, lines 22-26; 45-53). The waste products which may be cleaned using supercritical solutions include metal residues like metal residues of nitrides and silicon dioxide (see col. 4, lines 24-34). The supercritical solution can also include ammonium hydroxide (see col. 6, lines 24-28). The supercritical solution also comprises swelling agents which include tertiary amines like triethanolamine and these tertiary amines tend to break bonds in polymeric photoresists (see col. 8, lines 14-20) in a concentration range between about 0.1 and 15% by weight (see col. 9, lines 23-29). In the method of cleaning a wafer in a cleaning chamber with the supercritical cleaning solution, the temperature within the chamber is maintained at between about 50°C and 150°C, more preferably about 70°C, and preferably the contact time with at least one surface of the wafer is maintained for a period of between about 1 and 60 minutes, more preferably between about 5 and 20 minutes (see col. 13, lines 30-



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34; col. 11, lines 44-50). After treatment of the wafer with the supercritical solution, preferred methods further include rinsing the semiconductor with at least one of deionized water, an organic solvent, the supercritical solvent, and mixtures thereof (see col. 11, lines 53-57). Joyce, however, fails to disclose a binder which is derived from at least one ethylenically unsaturated reactant, for example polyvinyl alcohol or polyvinyl amine DeSimone teaches the features as described above.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate the amphiphilic species of DeSimone which contains a monomer segment like vinyl alcohol or amine segment into the supercritical cleaning solution of Joyce because this would remove a wide range of organic and inorganic material contaminants as taught by DeSimone.

12. Claims 1-16, 18, 20-41, 43, 45-54, 60-63 are rejected under 35 U.S.C. 103(a) as being unpatentable over Korzenski et al. (US Patent No. 6,943,139), hereinafter "Korzenski" in view of DeSimone.

The applied reference has a common inventor with the instant application. Based upon the earlier effective U.S. filing date of the reference, it constitutes prior art only under 35 U.S.C. 102(e). This rejection under 35 U.S.C. 103(a) might be overcome by: (1) a showing under 37 CFR 1.132 that any invention disclosed but not claimed in the reference was derived from the inventor of this application and is thus not an invention "by another"; (2) a showing of a date of invention for the claimed subject matter of the application which corresponds to subject matter disclosed but not claimed

in the reference, prior to the effective U.S. filing date of the reference under 37 CFR 1.131; or (3) an oath or declaration under 37 CFR 1.130 stating that the application and reference are currently owned by the same party and that the inventor named in the application is the prior inventor under 35 U.S.C. 104, together with a terminal disclaimer in accordance with 37 CFR 1.321(c). This rejection might also be overcome by showing that the reference is disqualified under 35 U.S.C. 103(c) as prior art in a rejection under 35 U.S.C. 103(a). See MPEP § 706.02(I)(1) and § 706.02(I)(2).

Korzenski teaches a particle contamination cleaning composition useful in semiconductor manufacturing for the removal of particle contamination from patterned silicon/silicon dioxide substrates having such particle contamination thereon (see col. 1, lines 8-14) comprising supercritical CO<sub>2</sub> (SCCO<sub>2</sub>), alcohol, fluorine source and optionally, hydroxyl additive, and in one aspect the composition comprises SCCO<sub>2</sub>, methanol, ammonium fluoride, fluorinated surfactant, and boric acid, wherein methanol is present at a concentration of from about 5 to about 20 wt%, fluoride is present at a concentration of from about 0.01 to about 2.0 wt%, and boric acid is present at a concentration of from about 0.01 to about 2.0 wt%, based on the total weight of the cleaning composition (see col. 1, line 59 to col. 2, line 3). The cleaning composition can be employed to contact a substrate having particulate contamination thereon at a pressure in a range of from about 1000 to about 7500 psi for sufficient time to effect the desired removal of the particulate contamination from the substrate, e.g., for a contacting time in range of from about 5 to about 30 minutes and a temperature of from about 35 to about 100°C (see col. 3, line 62 to col. 4, line 4). In one embodiment,

especially high removal of SiN particles from an Si/SiO<sub>2</sub> substrate was achieved by SCCO<sub>2</sub>/alcohol (15 wt%)/fluoride (0.55 wt%) solutions at a temperature and pressure of 55°C and 4000 psi, respectively, using a processing time of 30 minutes (10 minute dynamic flow, 10 minute static soak, 10 minute dynamic flow, followed by a three volume SCCO<sub>2</sub>/methanol (20 wt%) rinse and pure three volume SCCO<sub>2</sub> rinse), see col. 4, lines 5-12. The dynamic flow and static soak steps may be carried out alternately and repetitively (see col. 4, lines 13-20). Following the contacting of the cleaning composition with the substrate bearing the particulate contamination, the substrate thereafter preferably is washed with copious amounts of SCCO<sub>2</sub>/alcohol solution, e.g., 20% methanol solution, in a first washing step, to remove any residual precipitated chemical additives from the substrate region in which removal of particulate contamination has been effected, and finally with copious amounts of pure SCCO<sub>2</sub>, in a second washing step, to remove any residual alcohol co-solvent and/or precipitated chemical additives from the substrate region (see col. 4, lines 26-40). Korzenski, however, fails to specifically disclose a binder interactive with the silicon-containing particulate material to enhance removal thereof and water.

DeSimone teaches the features as described above.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to incorporate the amphiphilic species of DeSimone which contains a monomer segment like vinyl alcohol or amine segment, and water, into the cleaning composition of Korzenski because this would remove a wide range of organic and inorganic material contaminants as taught by DeSimone.

13. Claims 55, 58-59 are rejected under 35 U.S.C. 103(a) as being unpatentable over Clark et al. (US 2004/0171502), hereinafter "Clark".

Clark teaches processes for manufacturing semiconductor integrated circuits and, particularly, to the removal of etch residues and copper oxides from copper lines (see paragraph 0001 on page 1). The etch residues from a silicon wafer substrate are removed by using supercritical carbon dioxide in combination with a variety of chemically reactive agents soluble in supercritical carbon dioxide such as the solvents organic peroxides, ethers, organic bases, and strong organic and mineral acids (see paragraphs 0014 and 0016 on page 1). Carbon dioxide becomes supercritical at temperatures above 30°C and pressures above 1000 pounds per square inch, and a fluid is considered to be supercritical when it is no longer possible to return it to its liquid state by an increase in pressure (see paragraph 0011 on page 1). It is of course understood that the method is conducted at the above mentioned temperature and pressure ranges. In one embodiment, 10 milliliters of hydrogen peroxide and three drops of twenty-four percent ammonium fluoride in the supercritical carbon dioxide may be utilized (see paragraph 0025 on page 2). In some embodiments, co-solvents are added (see paragraph 0026 on page 2). Clark, however, fails to specifically disclose a pre-cleaning step comprising at least 95 wt% SCCO<sub>2</sub> and an oxidizing agent (like hydrogen peroxide) and a contacting step with a SCF-based composition comprising a SCF, at least one co-solvent, at least one etchant species.

It would have been obvious to one of ordinary skill in the art at the time the invention was made to remove etchant residues from the silicon wafer substrate of Clark with a composition comprising mainly supercritical carbon dioxide, 10 milliliters hydrogen peroxide, 3 drops ammonium fluoride, and a co-solvent because the teachings of Clark encompass these ingredients and proportions, and to repeat the step because it is within the level of ordinary skill in the art to repeat a step for effective cleaning.

#### ***Allowable Subject Matter***

14. Claims 55 and 57 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. The following is a statement of reasons for the indication of allowable subject matter: None of the prior art of record teaches, discloses or suggests a method as required in claim 55 wherein the SCF-based composition comprises the recited ingredients, or a method as required in claim 57 wherein the pre-cleaning formulation comprises ammonium hydroxide, t- butyl hydrogen peroxide and water.

#### ***Conclusion***

15. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure. The references are considered cumulative to or less material

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than those discussed above. In particular, US Patent 7,119,052 teaches similar disclosure as in Korzenski et al. (US Patent No. 6,943,139).

16. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Lorna M. Douyon whose telephone number is 571-272-1313. The examiner can normally be reached on Mondays-Fridays 8:00AM-4:30PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Harold Pyon can be reached on 571-272-1498. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Lorna M. Douyon/  
Primary Examiner  
Art Unit 1751

LMD  
10-15-07